Surprising reactions of a 2*H*-azaphosphirene complex with a silylene†

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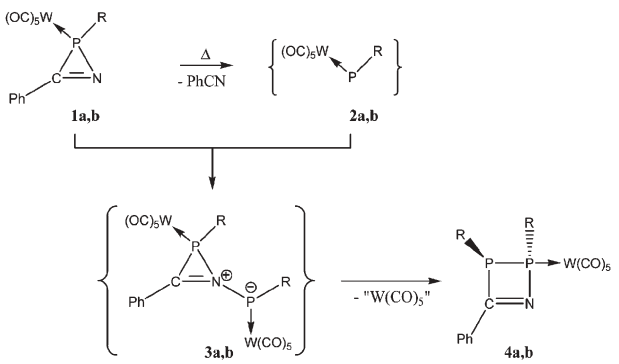
Reaction of the 2*H*-azaphosphirene complex 1 with the silylene 5 yielded the bicyclic carbene complex 9 as sole product at ambient temperature; the reaction was less selective at elevated temperatures; additionally, the synthesis and structure of the first 1,2,4,3-azadiphosphasilol-5-ene complex 11 is presented.

Recently, we reported on the formation of 2,3-dihydro-1,2,3-azadiphosphete complexes **4a**[1] and **4b**,[2] which were obtained by formal insertion of electrophilic terminal phosphinidene complexes **2a,b** into the three-membered ring of 2*H*-azaphosphirene complexes **1a,b**[3] (Scheme 1). Based on our assumptions that zwitterionic complexes **3a,b** are formed as intermediates, we became interested to study the reactivity of 2*H*-azaphosphirene complex **1a** towards other formal six-electron species, *e.g.*, silylenes.

Here, we report on the reaction of complex **1a**[3] with the thermally stable silylene (NN)Si: (formula in Scheme 2),[4] which was successfully used recently by Lammertsma and Gehrhus to achieve ring enlargement of 1*H*-phosphirene complexes.[5]

Reacting 2*H*-azaphosphirene complex **1a** with silylene **5** in benzene at ambient temperature furnished the bicyclic carbene complex **9**‡ as major product, having a carbene carbon atom connected to two heteroatoms as interesting structural motif (Scheme 2). Complex **9** was isolated in good yield (61.9%) and was characterized by NMR spectroscopy, MS spectrometry and X-ray crystallography.§ $^{31}P\{^{1}H\}$ NMR reaction monitoring showed that



Scheme 1 Ring-enlargement reactions of **1a,b** using transient phosphinidene complexes **2a,b** (**1a–4a**: R = $CH(SiMe_3)_2$, **1b–4b**: R = C_5Me_5).

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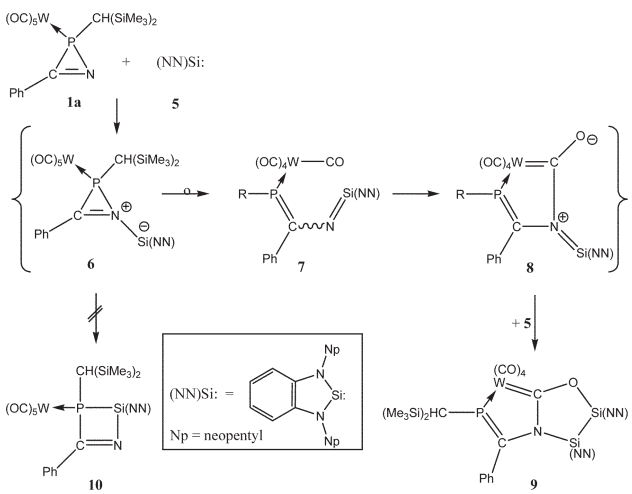
the formation of complex **9** was independent on the stoichiometry of **1** and **5**. Unfortunately, we gained no further insight into the reaction course and, therefore, we can only give a plausible explanation as shown in Scheme 2.

The primary formation of the Lewis acid–base adduct **6** seems reasonable as well as to assume that a rearrangement of **6** to the 2-aza-4-phospha-1-silabutadiene complex **7** may take place. Intramolecular attack of the nucleophilic nitrogen center in **7** to yield the zwitterionic carbene complex **8**, followed by rapid reaction with one equiv. of **5** and ring closure would then furnish complex **9**. It is remarkable that the 2,3-dihydro-1,2,3-azaphosphasilete complex **10** was not detected.

Complex **9** was characterized by multinuclear NMR spectroscopy and X-ray crystallography. **9** displayed a $^{31}P\{^{1}H\}$ resonance at 191.4 ppm ($^{1}J_{P,W}$ = 270.8 Hz) and a $^{13}C\{^{1}H\}$ resonance at 256.8 ppm for the carbene carbon atom, having a $^{2+3}J_{P,C}$ coupling constant magnitude of 9 Hz. In addition, a resonance at 171.0 ppm ($^{1}J_{P,C}$ = 41.2 Hz) was observed for the methylene carbon atom of the phosphaalkene moiety. The molecular structure of **9** (Fig. 1) contained the bicyclic structural unit with two folded five-membered rings. Remarkable is the planar arrangement of the W–C(5)–O(5)–Si(1) unit (torsion angle 179.2°).

The reaction between **1** and **5** was less selective at elevated temperatures (75 °C). Apart from phosphorus-containing products described earlier,[1] we observed the formation of two unidentified complexes as major products, with $^{31}P\{^{1}H\}$ resonances at 173.8 ($^{1}J_{P,W}$ = 272.1 Hz, *ca.* 33% by ^{31}P NMR integration) and 42.3 ppm ($^{1}J_{P,W}$ = 195.4 Hz, *ca.* 20%). The complex at 173.8 ppm was also formed if a benzene solution of the bicyclic compound **9** was heated, thus providing evidence that it relies on complex **9** as



Scheme 2 Proposed mechanism for the formation of **9**.

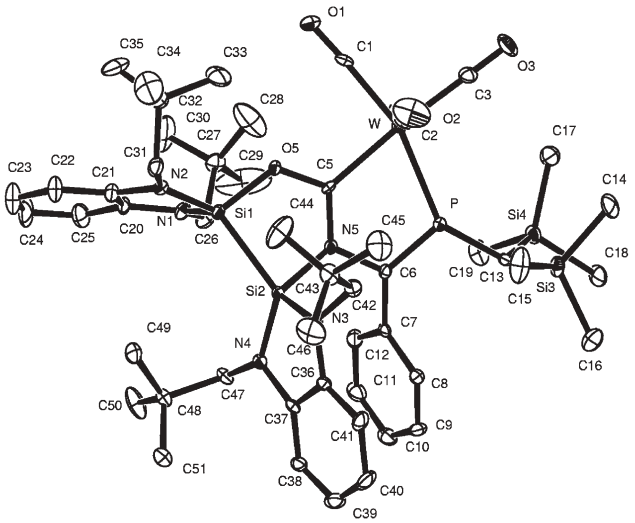
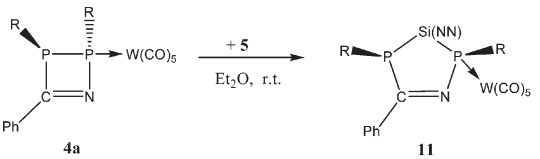


Fig. 1 Molecular structure of **9** in the crystal (thermal ellipsoids at 50% probability). Selected bond lengths (Å) and angles (°): W–C(5) 2.169(6), P–C(6) 1.689(6), W–P 2.4392(16), O(5)–C(5) 1.381(6), N(5)–C(5) 1.366(7); PC(6)N(5)Si(2) −141.9, WC(5)N(5)C(6) −1.8, C(5)N(5)C(6)P 10.1, Si(1)O(5)C(5)N(5) −2.9, O(5)C(5)N(5)Si(2) −27.3.



Scheme 3 Synthesis of complex **11**.

precursor. Unfortunately, these complexes could not be isolated using column chromatography. To get further insight into the reaction course at elevated temperatures, we decided to investigate the reactivity of complex **4a** towards **5**.

Therefore, we reacted pure **4a** with the silylene **5** in Et_2O and observed a clean reaction to the 1,2,4,3-azadiphosphasilol-5-ene complex **11** (Scheme 3).‡ Complex **11** was isolated in very good yield (90.1%) and was characterized by NMR spectroscopy, MS spectrometry and X-ray crystallography.§

The $^{31}P\{^1H\}$ NMR spectrum of **11** showed an AB-type spin system with resonances at 3.1 and −42.7 ppm ($^1J_{P,W}$ = 225.5 Hz) with a $^{2+3}J_{P,P}$ coupling constant magnitude of 211.1 Hz. In the $^{13}C\{^1H\}$ NMR spectrum, a doublet of doublets at 178.8 ppm ($J_{P,P}$ = 47.8 and 12.0 Hz) was observed for the ring carbon atom of the azadiphosphasilolene ring. The molecular structure of **11** in the crystal (Fig. 2) exhibited that, unlike in the precursor **5**, the bis(trimethylsilyl)methyl groups adopt *cis*-positions at the ring; this points to a non-concerted mechanism of the insertion reaction.

A comparison of some distances of **11** with related bonds of the dinuclear 2,3,4-triphenyl substituted 1,2,3,4-azatriphospholene tungsten complex[6] (**12**) suggest significant steric repulsions between the ring substituents at the P and Si centers in **11**, *e.g.*, 2.594(1) Å for P(1)–W(1) in **11** *vs.* 2.5154(8) and 2.5361(7) in **12** and 1.863(2) Å for P(2)–C(13) *vs.* 1.827(3) and 1.845(3).

Studies on the reactivity of 2*H*-azaphosphirene complexes towards other six-electron species such as carbenes are currently underway.

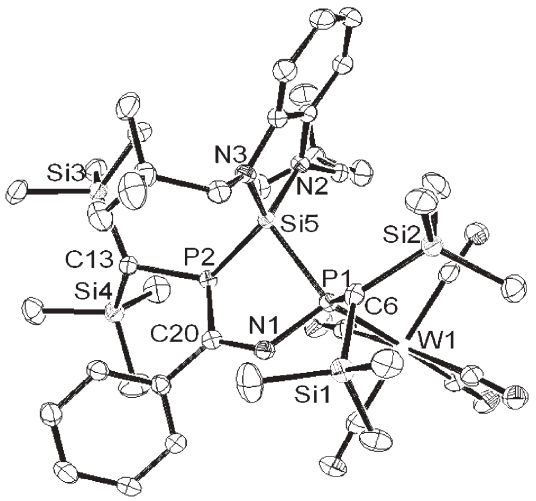


Fig. 2 Molecular structure of **11** in the crystal (thermal ellipsoids at 50% probability). Selected bond lengths (Å) and angles (°): P(1)–C(6) 1.847(2), P(1)–Si(5) 2.341(1), P(2)–Si(5) 2.258(1); P(1)–Si(5)–P(2) 86.57(3), Si(5)–P(2)–C(20) 92.3(1), N(1)–P(1)–Si(5) 94.8(1).

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Notes and references

‡ Satisfactory elemental analysis data were obtained for complexes **9** and **11**. NMR data were recorded in C_6D_6 solutions on a Bruker AX 300 spectrometer for **9** (300.1 MHz for ^1H, 75.0 MHz for ^{13}C, 59.5 MHz for ^{29}Si and 121.5 MHz for ^{31}P) and on a Bruker AMX spectrometer for **11**(500.1 MHz for ^1H, 125.76 MHz for ^{13}C, 99.3 MHz for ^{29}Si and 202.5 MHz for ^{31}P), using tetramethylsilane and 85% H_3PO_4 as standard references. Chemical shifts δ are given in ppm, coupling constant magnitudes J in Hz. *Selected NMR data* of **9**: ^1H NMR (C_6D_6, 500.0 MHz): δ 0.18 (s, 18H, $SiMe_3$), 0.86 (s, 18H, $C(CH_3)_3$), 1.18 (s, 18H, $C(CH_3)_3$), 2.08 (d, 1H, $^2J_{P,H}$ = 18.3 Hz, $CH(SiMe_3)_2$), 2.78 (d, 1H, $^2J_{H,H}$ = 14.5 Hz, $CH_2C(CH_3)_3$), 3.15 (d, 1H, $^2J_{H,H}$ = 14.3 Hz, $CH_2C(CH_3)_3$), 3.33 (d, 1H, $^2J_{H,H}$ = 14.5 Hz, $CH_2C(CH_3)_3$), 3.51 (d, 1H, $^2J_{H,H}$ = 14.3 Hz, $CH_2C(CH_3)_3$), 6.30 (m_c, 2H, Ph), 6.57 (m_c, 2H, Ph), 6.71 (m_c, 1H, Ph), 6.78 (m_c, 4H, Ph), 6.85 (m_c, 4H, Ph). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.76 MHz): δ 1.32 (s, $SiMe_3$), 17.7 (d, $^1J_{P,C}$ = 37.5 Hz, $CH(SiMe_3)_2$), 29.2 (s, $C(CH_3)_3$), 29.5 (s, $C(CH_3)_3$), 34.5 (s, $C(CH_3)_3$), 35.0 (s, $C(CH_3)_3$), 54.0 (s, CH_2), 54.4 (s, CH_2), 110.0 (s, C_{arom}), 111.9 (s, C-Ph), 118.3 (s, C-Ph), 118.7 (s, C-Ph), 126.8 (s, C-Ph), 128.3 (s, C-Ph), 128.8 (s, C-Ph), 138.0 (s, C-Ph), 138.8 (s, C-Ph), 171.0 (d, $^1J_{P,C}$ = 41.2 Hz, P=C), 205.7 (br, CO), 256.8 ($^{2+3}J_{P,C}$ = 9 Hz, W=C). $^{29}Si\{^1H\}$ NMR (C_6D_6, 99.3 MHz): δ −35.3 (s, COSi), −30.7 (d, $^3J_{P,Si}$ = 8.8 Hz, CNSi), 3.6 (d, $^2J_{P,Si}$ = 5.9 Hz, $SiMe_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.51 MHz): 191.4 (s_{sat}, $^1J_{P,W}$ = 270.8 Hz). *Selected NMR data* for **11**: ^1H NMR (C_6D_6, 300.1 MHz): δ −0.08 (s, 9H, $SiMe_3$), −0.03 (s, 9H, $SiMe_3$), 0.29 (s, 9H, $SiMe_3$), 0.41 (s, 9H, $SiMe_3$), 1.15 (s, 9H, $C(CH_3)_3$), 1.20 (s, 9H, $C(CH_3)_3$), 1.96 (dd, 1H, $^2J_{P,H}$ = 19.6, $^4J_{P,H}$ = 2.1 Hz, $CH(SiMe_3)_2$), 2.25 (dd, 1H, $^2J_{P,H}$ = 8.6, $^4J_{P,H}$ = 1.0 Hz, $CH(SiMe_3)_2$), 3.17 (d, 1H, $^2J_{H,H}$ = 14.1 Hz, $CH_2C(CH_3)_3$), 3.43 (d, 1H, $^2J_{H,H}$ = 14.1 Hz, $CH_2C(CH_3)_3$), 3.54 (d, 1H, $^2J_{H,H}$ = 14.6 Hz, $CH_2C(CH_3)_3$), 4.15 (d, 1H, $^2J_{H,H}$ = 14.6 Hz, $CH_2C(CH_3)_3$), 6.7–6.9 (m_c, 4H, H-Ph), 7.0–7.2 (m_c, 5H, H-Ph). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.0 MHz): δ −0.5 (d, $^3J_{P,C}$ = 6.5 Hz, $SiMe_3$), 1.0 (d, $^3J_{P,C}$ = 4.5 Hz, $SiMe_3$), 2.5 (s, $SiMe_3$), 3.2 (d, $^3J_{P,C}$ = 1.3 Hz, $SiMe_3$), 17.8 (d, $^1J_{P,C}$ = 17.8 Hz, $CH(SiMe_3)_2$), 27.9 (d, $^1J_{P,C}$ = 3.2 Hz, $CH(SiMe_3)_2$), 28.8 (s, $C(CH_3)_3$), 28.9 (s, $C(CH_3)_3$), 33.6 (s, $C(CH_3)_3$), 34.3 (s, $C(CH_3)_3$), 55.7 (s, $CH_2C(CH_3)_3$), 57.6 ($CH_2C(CH_3)_3$), 107.7 (s, C-Ph), 108.9 (s, C-Ph), 110.6 (s, C-Ph), 116.8 (s, C-Ph), 117.5 (s, C-Ph), 118.2 (s, C-Ph), 127.5 (s, C-Ph), 127.9 (s, C-Ph), 128.4 (s, C-Ph), 138.7 (s, C-Ph), 139.5 (s, C-Ph), 140.5 (s, C-Ph), 178.8 (dd, $^{1+4}J_{P,C}$ = 47.8, $^{2+3}J_{P,C}$ = 12.0, PCNPSi), 195.7 (d, $^2J_{P,C}$ = 21.7 Hz, *trans*-CO), 197.8 (dd_{sat}, $^2J_{P,C}$ = 5.8, $^4J_{P,C}$ = 1.9, $^1J_{W,C}$ = 126.4 Hz, *cis*-CO). $^{29}Si\{^1H\}$ NMR (C_6D_6, 59.5 MHz): δ −0.8 (d, $^2J_{P,Si}$ = 12.0 Hz, $SiMe_3$), 0.8 (dd, $^{1+4}J_{P,Si}$ = 48.7, $^{1+4}J_{P,Si}$ = 6.2 Hz, PSiP), 2.6 (pt, $^2J_{P,Si}$ = 6.9 Hz, $SiMe_3$),

4.1 (d, $^{2}J_{P,Si}$ = 7.4 Hz, $SiMe_3$), 4.4 (dd, $^{2}J_{P,Si}$ = 19.4, $^{4}J_{P,Si}$ = 1.8 Hz, $SiMe_3$). ^{31}P NMR (C_6D_6, 121.5 MHz): δ 3.1 (d_{sat}, $^{2+3}J_{P,P}$ = 211.1, $^{1}J_{P,W}$ = 225.5, $^{2}J_{P,H}$ = 18.6 Hz, σ^4-P), −42.7 (d, $^{2+3}J_{P,P}$ = 211.1, $^{2}J_{P,H}$ = 3.8 Hz, σ^3-P).

§ *Crystal structure determination* for **9**: $C_{51}H_{76}N_5O_5PSi_4W$. *Crystal data*: orthorhombic, space group $P2_12_12_1$ (no. 19), a = 12.9763(2), b = 17.5048(3), c = 25.6015(4) Å, U = 5815.3(2) Å^3, Z = 4, T = 223(2) K. *Data collection*: a red crystal *ca*. 0.10 × 0.10 × 0.05 mm was used to record 25183 intensities on a Nonius KappaCCD diffractometer (Mo-Kα radiation, $2\theta_{max}$ = 50°). Absorption corrections were applied using MULTISCAN. *Structure refinement*: the structure was refined full-matrix least squares on F^2 (SHELXL-97, G. M. Sheldrick, Univ. Göttingen) to $wR2$ = 0.076, $R1$ =0.055 for 604 parameters, 0 restraints and 9729 unique reflections; S = −0.026(6), max./min. $\Delta\rho$ 0.53 and −0.58 e Å^{-3}. The hydrogens were refined using a riding model. *Crystal structure determination* for **11**: $C_{42}H_{69}N_3O_5P_2Si_5W{\cdot}0.5Et_2O$. *Crystal data*: monoclinic, space group $P2_1/n$ (no. 14), a = 11.3153(1), b = 19.0877(2), c = 25.1500(3) Å, β = 93.196(1)°, U = 5423.53(10) Å^3, Z = 4, μ(Mo-Kα) = 2.342 mm^{-1}, T = 123(2) K. *Data collection*: a yellow crystal *ca*. 0.30 × 0.20 × 0.15 mm was used to record 43997 intensities on a Nonius KappaCCD diffractometer (Mo-Kα radiation, $2\theta_{max}$ = 60°). An empirical absorption correction was applied (min./max. transmission = 0.55337/0.65097). *Structure refinement*: the structure was refined as above to $wR2$ = 0.0647, $R1$ = 0.0275 (for $I > 2\sigma(I)$) for 543 parameters, 17 restraints and 12333 unique reflections; max./min. $\Delta\rho$ 1.577/−1.488 e Å^{-3}. The hydrogens were refined using a riding model. CCDC 278009 and 278010. See http://dx.doi.org/10.1039/b509567k for crystallographic data in CIF or other electronic format.

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